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SUMMARY OF U.S. LIMB TECHNOLOGY

by

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16. ABSTRACT The paper summarizes the development of limestone injection multistage burner (LIMB) technology in the U.S. Among many control processes tested in the U.S. for conformance with New Source Performance Standards (NSPS) was the injection of limestone into the furnace region of power boilers to capture sulfur oxides (SOx). These limestone injection removals never achieved NSPS levels, but its relative simplicity encouraged continued interest. When multistage burners were developed for nitrogen oxides (NOx) control, it was natural to try combining them with limestone injection: the combination showed improved capture. Initially the improved capture and the benefit of combined SOx/NOx control gave impetus to a study of limestone injection with multistage burners (LIMB). In addition, it also became apparent that acid rain control strategies could be made more cost effective with a very simple process like LIMB, even if the process could not achieve NSPS control levels. The resulting EPA LIMB technology development program consists of several activities which, in large measure, have proceeded in parallel: (1) fundamental research, focusing on the kinetics of potential LIMB reactions and on properties of limestone and limestone products; (2) pilot scale research; (3) modeling; (4) engineering and cost analyses; and (5) process demonstration and commercial utilization.

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Limestone	Acidification	Stationary Sources	08G	07C
Coal		LIMB Technology	21D	
Burners		Acid Rain	13A	
Sulfur Oxides		Limestone Injection	07B	
Nitrogen Oxides		Multistage Burners		

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INTRODUCTION

During the 1960's and 1970's, the United States became increasingly aware of the need for clean air and enacted legislation to lower ambient concentrations of air pollutants and to reduce emissions from major sources. The latter was to be applied to new sources and hence produced New Source Performance Standards (NSPS). Levels of control required by NSPS were typically 90 percent but in some cases were as low as 70 percent. Among many control processes tested for NSPS was the injection of limestone into the furnace region of power boilers to capture sulfur oxides (SO_x). These limestone injection removals never achieved NSPS levels[1] but its relative simplicity encouraged continued interest. When multistage burners were developed for nitrogen oxides (NO_x) control,[2] it was natural to try combining them with limestone injection: the combination showed improved capture. Initially, the improved capture and the benefit of combined SO_x/NO_x control gave impetus to a study of limestone injection with multistage burners (LIMB).[3] In addition, it also became apparent that acid rain control strategies could be made more cost effective with a very simple process like LIMB even if the process could not achieve NSPS control levels. Consequently, the Environmental Protection Agency (EPA) formulated a program to develop LIMB technology.[4,5]

The EPA LIMB program consists of several activities which in large measure have proceeded in parallel. First is fundamental research which has focused on the kinetics of potential LIMB reactions (e.g., calcination and sulfation) and on properties of limestone and limestone products to identify and optimize properties providing high reactivity for SO_x capture. Second is pilot scale research which has provided information on the effect of the furnace conditions on LIMB and on the effect of LIMB on furnace operation and on the operation of electrostatic precipitators (ESPs). Results from these first two activities have been analyzed and extrapolated by a third activity, modeling. Modeling has proven extremely useful for filling in the total picture of parametric effects and for testing theories. Modeling

leads to a fourth activity, engineering and cost analysis. Lastly, is process demonstration and commercial utilization. The results of work in these areas of activity are the subject of this paper.

FUNDAMENTAL RESEARCH

KINETICS

Many possible reactions were investigated including those of limestone and reagents made from limestone with reduced sulfur species. However, results from pilot scale work indicate the relative unimportance of reduced sulfur species in total sulfur capture, even with multistage burners which have a distinct reducing zone. Other reactions which are relatively unimportant are the direct reaction between limestone and sulfur dioxide (SO_2) and the reaction of magnesium oxides with SO_2. Two important conclusions from this are:

1) The limestone must calcine to calcium oxide before it can react to capture SO_2; and

2) The magnesium oxide fraction of a dolomite does not contribute to the capture of SO_2 with a dolomite.

Consequently, the two main reactions are the calcination of limestone to calcium oxide (lime) and the sulfation of lime. It has been determined that the calcination rate is 25 n mol/cm^2-s at 670°C, and that the activation energy is 49 kcal/mol. For sulfation, the reaction is apparently controlled by product layer diffusion with a diffusivity of 21 x 10^{-9} cm^2/s and an activation energy of 33 kcal/mol. Sulfation rates increased with the 0.64 power of SO_2 concentration.

SORBENT PROPERTIES

Although the original concept was to use limestone, many reagents made from limestone have been considered as sorbents for SO_x. Among those re-

ceiving the greatest attention have been precalcined high-surface-area lime, atmospheric hydrates of lime, pressure hydrates of lime, and promoted varieties of all of the above. Interest in different sorbent types arose from pilot-scale research findings that surface area and particle size have a significant effect on reactivity.

While uncalcined limestone generally has a surface area less than 3 m^2/g, hydrates naturally have surface areas from 12 to 25 m^2/g. By precalcining the limestone, even greater surface areas can be achieved; e.g., 80 m^2/g. Unfortunately, larger surface areas before injection do not always translate into larger surface areas in the furnace, because newly formed calcium oxide sinters and loses surface area rapidly at furnace temperatures. When there is more than 1 sec residence time in the temperature zone for sulfation, it has been found that precalcined limes (even with very large surface areas) do not have an advantage over limestone. At very short times (less than 0.5 sec), the limestones are less reactive than the precalcines because the limestones need some time for calcination and too little time is left for sulfation.

The advantage of hydrates appears to be their inherently small particle size. Finely ground limestone might be 100 percent less than 325 mesh or 44 μm. The mass median diameter of such limestone might be 10 to 20 μm. Only with expense and difficulty is limestone ground much finer than this. However, hydrates typically have mass median diameters of 3 to 6 μm. Moreover, it appears that hydrate particles are actually agglomerates of very fine particles which may be as small as 0.1 μm. Consequently, the hydrates are far more reactive than limestones. Within the category of hydrate there also can be differences in reactivity. While no great difference has been found for atmospheric vs. pressure slaked hydrates, water slaking is preferable to steam slaking, and the temperature of the hydration water also has an effect.

Promoters can play a role in the effectiveness of a sorbent, but are of second-order importance to selection of the type of sorbent and optimization of reactivity for that sorbent. Large effects of promoters can be demonstrated in systems or during firing without fly ash. Unfortunately, the presence of fly ash appears to provide competing surface area to absorb the promoter before the promoter can enhance the sorbent. Two classes of promoters have been studied primarily: alkali metal carbonates (e.g., sodium carbonate) and group VIa metal oxides (e.g., chromium oxide). The fundamentals of promotion are not yet understood but are thought to be related to modification of the product layer (sulfate layer) to increase diffusivity of sulfur species to the reactive layer of the calcium oxide.

PILOT SCALE RESEARCH

FURNACE EFFECTS ON LIMB

Many conditions of the furnace or of the furnace region of a power boiler have a potential impact on LIMB. Some of these are the furnace firing rate (or boiler load), the temperature profile, the velocity profile, and the temperature and mixing conditions at the point of injection. Pilot scale research has been quite consistent in showing greater SO_2 capture at lower firing rates. In general, lower firing rates mean lower gas flow through the furnace and hence greater residence in the furnace. Consequently, at lower firing rates the limestone has more time in which to react with SO_x. The effect of temperature profile is also linked to time for the limestone to react. If heat is extracted from the furnace very rapidly, the temperature profile is steep and the residence time of limestone at temperatures favorable for reaction will be short. The steepness of the temperature profile is referred to as quench rate measured in degrees per second. The higher the quench rate, the less time for reaction and the lower the sulfur capture. With some sorbents, such as limestone, there are other problems (e.g., the formation of a sulfate shell) which limit the reactivity more severely than high quench rates. Thus limestone reactivity is not greatly impacted by quench rate. With highly reactive hydrates, however, 20 to 40 percent of the reactivity may be lost at high quench rates. The effect of velocity profile

is to determine the dispersion of sorbent throughout the furnace after injection. As an extreme example of this effect is the difference between injection into wall-fired and tangentially fired boilers. The effect of injection conditions is seen via the subsequent reactivity of the sorbent and the residence time of the sorbent in the reactive temperature zone. If the injection location is too close to the burners, the temperature will be too high and the newly formed calcium oxide will sinter to a less reactive state. If the injection location is too far from the burners, there will be insufficient time for sulfation.

EFFECT OF LIMB ON THE FURNACE AND ESP

The main concern for the effect of LIMB on the furnace is the formation of deposits on the convective heat transfer surfaces or fouling. Fouling tests take extended periods of operation so that little data on actual fouling is available. Naturally, the amount of material depositing on the convective surfaces is greater because there is more material going through the furnace (limestone in addition to fly ash). It has been shown that deposits formed during limestone injection are soft and may be dislodged by ordinary soot blowers. It is expected that fouling problems may be prevented by merely increasing the soot blowing capacity.

The effect of LIMB on the electrostatic precipitator (ESP) is twofold: 1) the loading to the ESP is increased, and 2) the resistivity of the ash is increased. Increasing resistivity decreases the operating range and the effectiveness of the ESP and must be avoided. Resistivity is easily lowered with conditioning agents such as sulfur trioxide or water vapor. The addition of water vapor also has the effect of lowering the gas temperature, which also lowers the resistivity. It has been shown that LIMB fly ashes are easily conditioned so that the resistivity problem has a ready solution. The problem of increased loading, however, must be met with either a modified ESP design which is more effective or increased collection from a precollector or from additional area in the ESP.

MODELING

A number of models have been developed for different purposes and based on different assumptions. Some of the models developed include: 1) a heat transfer model to determine the temperatures in the boiler and the temperature response of injected particles, 2) a mixing model to calculate the contact between injected particles and SO_x, and 3) a reaction model which simulates the utilization of a single particle of alkali with SO_x. Each of these models has different versions according to the assumptions used. For example, the reaction model can be based on describing the particle as an agglomeration of grains, as a solid with random pores, or as a solid with pores in a pore tree structure. Moreover, other assumptions may be made concerning the controlling reaction rate and the kinetics data which describe it.

In spite of the large number of different possible versions of these models, certain consistent insights have been gained through modeling. For example, the reaction model has been used to clarify the relative effect of surface area and particle size on reactivity. While it had been established that surface area was the predominant parameter controlling sorbent reactivity, it was not clear what relationship sorbent particle size had to reactivity or how surface area and particle size were interrelated. Modeling revealed that particle size acts as a limiting factor because of pore diffusion. If the particle is very small (less than 1 μm), it has a small effect on sorbent reactivity, and surface area controls the sorbent reactivity. As the particle size increases for a given mass, less particle surface area is readily available and SO_2 must diffuse through pores to reach the surface area. Hence, when the particle is very large, the pore diffusion becomes the limiting factor, and surface area has little effect. Of course, with very large particles the sorbent reactivity is also very small so that large particles are not of interest. The particle size should be made as small as economically possible to avoid the pore diffusion limitation and utilize the full reactivity of the surface area generated by the chosen sorbent.

ENGINEERING AND COST ANALYSIS

Activity has been focused on the cost tradeoffs between LIMB and flue gas desulfurization (FGD). Cost and sensitivity analyses were conducted to evaluate the effect of: coal sulfur content, boiler capacity factor, sorbent cost, boiler size, retrofittability (for FGD systems), and book life. The strategy used for analysis was to evaluate the unit control cost of wet FGD, dry FGD, and LIMB at a base case and then vary each of the above parameters around the base case. For the base cases, the data indicate that the capital charge component of the total levelized annual revenue requirement is 48, 55, and 29 percent for wet FGD, dry FGD, and LIMB, respectively, thus indicating that LIMB is less capital cost intensive than FGD. Wet and dry FGD are 34 and 12 percent more expensive, respectively, than LIMB when expressed in \$/ton of SO_2 removed, while they are 125 and 89 percent more expensive, respectively, than LIMB when expressed in mills/kWh. LIMB at 50 percent removal results in fewer tons of SO_2 removed than do either wet or dry FGD at NSPS levels; consequently, when the total cost is distributed over tons of SO_2 removed, LIMB's cost advantage is not as great as when the total cost is distributed over a constant amount of electrical energy produced.

UNIT CONTROL COST VS. COAL SULFUR

It should be noted that NSPS levels were assumed for both wet and dry FGD, while constant removal percentages were assumed for LIMB. NSPS require at least 70 percent removal, emissions of not more than 1.2 lb SO_2 per million* Btu, and a lower SO_2 emission limit of 0.6 lb SO_2 per million Btu, thus resulting in a sliding scale of SO_2 removal as shown below:

1.5% S: 76.2% SO_2 removal,
2.2% S: 83.8% SO_2 removal, and
3.0% S: 88.1% SO_2 removal

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* To convert to ng/J from $lb/10^6$ Btu, multiply by 433.

LIMB at 50 percent SO_2 removal exhibits lower cost per ton of SO_2 removed than both wet and dry FGD up to about 2.6 percent sulfur. Beyond this point, there is a crossover, with dry FGD showing a slight advantage over LIMB. LIMB at 60 percent SO_2 removal is also shown for situations where this improved performance might result from higher sorbent activity and more favorable boiler conditions such as residence time in the sulfation window. This 60 percent SO_2 removal LIMB case assumed no increase in stoichiometry or sorbent cost, but it might be the result of technology improvements only. For this situation, LIMB exhibits consistently lower control costs than either wet or dry FGD. LIMB's cost advantage is especially evident for the mid-range sulfur and lower sulfur coals.

UNIT CONTROL COST VS. CAPACITY FACTOR

Similar behavior is displayed by each of the three technologies in that control costs decrease as boiler capacity factor increases. However, the effect of capacity factor is more pronounced for wet and dry FGD than for LIMB. Increasing the capacity factor from 35 to 65 percent results in a reduction in control cost of 39, 38, and 24 percent for wet FGD, dry FGD, and LIMB, respectively. This is primarily attributed to FGD systems being more capital cost intensive than LIMB. Consequently, as more SO_2 is removed as a result of increased plant utilization, these larger capital costs become a smaller portion of the control cost ($/ton SO_2 removed).

UNIT CONTROL COST VS. SORBENT COST

As expected, control costs increase as sorbent costs increase; however, this is more pronounced for LIMB than for wet or dry FGD since LIMB is more O&M cost intensive, and the cost of sorbent makes up a large portion of these costs. Increasing the hydrated lime cost from 55 to 85 $/ton results in an increase in control cost of 5 and 24 percent, for dry FGD and LIMB, respectively. With wet FGD, a 50 percent increase in limestone cost, from 12 to 18 $/ton, results in only a 2 percent increase in unit control cost. Since

sorbent utilization is greater for wet and dry FGD, and since FGD systems are more capital cost intensive than LIMB, sorbent cost is not as dominant a factor for FGD.

PROCESS DEMONSTRATION

The basic goal of the LIMB Demonstration is to extend the LIMB technology development to a full-scale application on a wall-fired utility boiler. By co-funding such a demonstration with industry, EPA hopes to encourage the acceptance and ultimate commercialization of this technology in the shortest possible time.

The successful retrofit of LIMB to an existing boiler is expected to demonstrate that (a) reductions of 50 to 60 percent in SO_x and NO_x emissions can be achieved at a fraction of the cost of add-on FGD systems, (b) boiler reliability, operability, and steam production can be maintained at levels existing prior to LIMB retrofit, and (c) technical difficulties attributable to LIMB operation--such as additional slagging and fouling, changes in ash disposal requirements, and an increased particulate load--can be resolved in a cost-effective manner.

As a first step toward achieving this goal, EPA requested and received proposals for a full-scale utility size demonstration of LIMB. A proposal from Babcock & Wilcox (B&W), a major utility boiler manufacturer located in Alliance, Ohio, was selected for contract award. B&W proposes a 3-1/2 year project that includes design and installation of a LIMB system at Ohio Edison's 105 MW coal-fired Edgewater Station in Lorain, Ohio, and a full year of operating and testing to demonstrate its capabilities. EPA will share the cost of the project with the major project participants--B&W, Ohio Edison, the State of Ohio, Stone & Webster Engineering, and Radian Corporation.

A two-part program has been devised to provide a full characterization of the LIMB retrofit. A baseline test will be made early in the project to quantify and document normal operations that occur in the absence of LIMB. The baseline test will include a rigorous test program of on-site measurements coupled with an analysis of historical boiler records. Following system start-up and documentation, a 1-year performance test will be made to measure all aspects of LIMB performance.

Emissions during the 1-year test period will be measured to establish long-term emission characteristics of the system. The 1-year test period will include three 30-day test sequences when full emission testing will be conducted with optimum LIMB operating conditions. These measurements will include continuous monitoring of SO_x, NO_x, CO, CO_2, O_2, and hydrocarbons using standard EPA sampling and analysis methods. Particulate mass, composition, and size distribution before and after the electrostatic precipitator (ESP) will also be measured manually at frequent intervals. Other parameters, such as fuel composition and continuous recording of boiler operating conditions, will be measured to enable correlation of emissions with parameters that affect emissions.

Continuous monitoring and/or documentation of steam production, operating time, and outages will be conducted during the 1-year test to evaluate the effects of sorbent injection on boiler performance and reliability. Slagging and fouling characteristics during LIMB operation will be determined in tests collecting and evaluating operating data such as steam temperature and pressure drop, visual inspection of radiant and convective sections, and direct measurement of buildup on steam tubes. The extent of corrosion and erosion will be determined by visual inspection and measurement of tubewall thickness at frequent intervals. Solid deposition on furnace walls and tube surfaces will be sampled and analyzed to further identify and quantify problem areas. In addition, flue gas temperatures will be monitored at several points to characterize the boiler thermal environment.

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